ARPA-E Challenge: High Gas Mass Transfer for Bio-Based Reactors

Source: InnoCentive **Challenge ID:** 9933437 **Type:** Ideation

ABSTRACT

This submission presents a continuous balanced flow fluidized bubble reactor without use of conventional stirrer and that involves no support for microbes. Reactants and nutrients are continuously fed in from the reactor bottom and end products are continuously removed from the reactor top. Efficient mass transfer is achieved by use of low-medium intensity ultrasound waves by use of several low power transducers installed inside the reactor. Microbes/Enzymes migrate to areas of low ultrasound fields and are thus segregated into areas of low ultrasound field. Undulating ultrasound field is created by ultrasound waves interfering with its reflection to create standing waves creating areas of low and high strengths, low field strength areas richer in microbial mass while high field strength areas richer in gas bubble because of their introduction in such areas. High ultrasound field in such areas subject gas bubbles to repeated caviatation and aids its movement into areas richer in microbial mass and through cell walls by reversible cavitation of microbial cell walls. Total gas volume of gas bubbles present in reactor at any time is more than volume of liquid as would be seen later is one requirement of efficient mass-transfer. Flow of gases introduced into the reactor bottom and flows upwards though bubble trays and balances weight of liquid present in the reactor. Liquid end products formed are removed from reactor top continuously so that weight of liquid hold-up in the reactor remains constant during course of a reaction. Ultrasound improves Gas-Liquid mass transfer coefficient *ka* by a factor of at least 10. These bubble reactors convert only a small fraction of input gases into finished products during a single pass through the reactor and maintain agitation in unstirred reactors needed for effective mass transfer, ultrasound improves out-gassing significantly thus improving overall mass-transfer rates. Data presented at the end of the submission demonstrates that mass-transfer coefficients obtained are far superior to values set in solution requirements. Exiting gases are scrubbed to remove Carbon Dioxide and recycled back to the column after a make-up with balancing gases so that a constant and high flow rate of gases maintained to counterbalance the weight of liquid present in the column. Reversible cavitation due to ultrasound leads to faster turnover of gases to liquid end products by microbes. Microbes seem to work harder due to irradiation by ultrasound and carry end product by out-gassing back to liquid phase from which it can be continuously scrubbed. Nutrients are also introduced at the reactor bottom in such a quantity that during its transition to the reactor top it is entirely during its transit to the reactor top.

Introduction

This submission proposes use of ultrasonic waves of 20-50 KHz range of moderate power (maximum 60 W for a test reactor volume of 1 lit and power levels of even 50 % can do equally

effective job in these types of bubble reactors). Actual power dissipation in such volumes is about 60 % of incident ultrasonic power and has been established that it leads to increase gas-liquid mass-transfer coefficients by an order of magnitude in stirred/unstirred reactor bench top test reactors. Biotech reactors are characterized by use of low speed stirred reactors of very high holding capacities. Slow speed stirring is often necessary to avoid damage to intact cells due to fragility of microbial cell walls at high terminal velocities at impeller tip in reactors with large diameter/very high volumes and are generally mass-transfer limited due of this design requirement.

Application of ultrasound to biotechnology is relatively new, but several processes that take place in the presence of cells or enzymes are activated by ultrasonic waves. High intensity ultrasonic waves break the cells walls and denaturize enzymes. Low intensity ultrasonic waves can modify cellular metabolism or improve the mass transfer of reagents and products through the boundary layer or through the cellular wall and membrane. In case of enzymes, the increase in the mass transfer rate of the reagents to the active site seems to be the most important factor. Immobilized enzymes are more resistant to thermal deactivation produced by ultrasound than native enzymes. Reverse micelles can be used to carry out synthesis using enzymes. Several applications of ultrasound to the biotechnology are discussed by authors (1). Microbes seem to work harder when irradiated with low/medium power ultrasonic radiation.

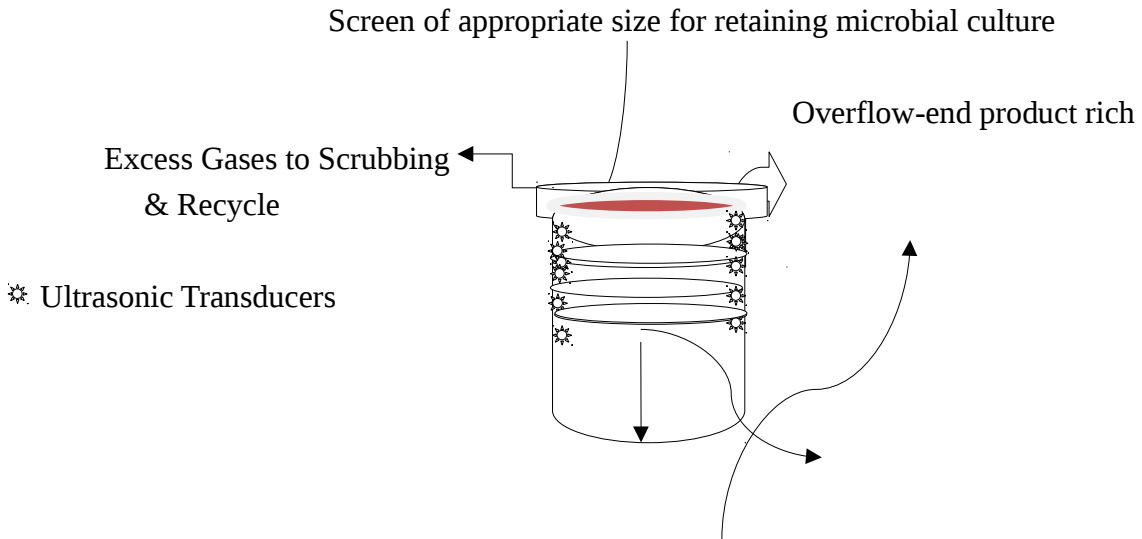
Enhanced metabolic productivity of microbial, plant and animal cells in bioreactors can greatly improve the economics of biotechnology processes. Ultrasound is one method of intensifying the performance of live biocatalysts. Ultrasonication is generally associated with damage to cells but evidence is emerging for beneficial effects of controlled sonication on conversions catalyzed by live cells, authors focus (2) on the productivity enhancing effects of ultrasound on live biological systems and the design considerations for sonobioreactors required for ultrasound-enhanced bio-catalysis in this review.

F.Laugier et al (3) present a detailed study of effect of medium power ultrasonic waves in improvement mass-transfer of gases into liquid in a test reactor. The effect of ultrasound on the pseudo-solubility of nitrogen in water and on gas-liquid mass transfer kinetics has been investigated in an autoclave reactor equipped with a gas inducing impeller. In order to use organic liquids and to investigate the effect of pressure, gas-liquid mass transfer coefficient was calculated from the evolution of autoclave pressure during gas absorption to avoid any side-effects of ultrasound on the concentrations measurements. Ultrasound effect on the apparent solubility is very low (below 12%). These authors use a complicated mechanism for gas introduction by use of low pressure draught created at trailing edge of a rotating impeller containing holes for supply of gas through a hollow rotor. Introduction of gas in the system takes place as a result of rotation of stirrer and rate of flow of gas is called gas induction speed. Ultrasound greatly improves gas-liquid mass transfer as evidenced from a factor of ten improvements in *ka* values, especially at low gas induction speed (slow stirrer rotational speed and small volume of gas introduction), this improvement being boosted by pressure, the

difference between *ka* values in absence/presence of ultrasound are highest at low stirring speeds- low gas induction rates. In typical conditions of organic synthesis: 323 K, 1100 rpm, 10 bar, k(L).a is multiplied by 11 with ultrasound (20 kHz/62.6 W).

The impact of sonication is much higher on gassing out than on gassing in. Under identical conditions this enhancement is at least five times higher for degassing, ultrasonic degassers are quite common and are commonly used for degassing liquids. Authors (3) have used a reactor in which gas induction into the system takes place as a result of stirring due to low pressure draft created at trailing edge as a result of movement of stirrer blade through hole placed at the back of a rotating stirrer blade, an ingenious arrangement for introduction of gas into a system but one that which needlessly complicates the interpretations results, but their findings are quite instructive. If one were to interpret results at low stirring speed, also characterized by low gas induction due to this correlation between stirring speed and gas induction volume, improvements are quite impressive and are related to net ultrasonic power coupled in to the system. When using low speed gas induction improvements to *ka* values for low and medium power range vary from 0.0005 to 0.01 and 0.02 respectively. Improvements between no ultrasonic power to low ultrasonic power are substantial (x20 times) in cases of low stirring speed/low stirring speed/low agitation and is not related linearly to coupled ultrasonic power, incremental increase in values mass-transfer co-efficient with increase in power follows a non-linear relationship. On a pro-rata basis initial applied ultrasonic power has substantially higher efficacy in increase of mass –transfer than when using increased above and beyond this small initial applied power a result akin to saturation.

Ultrasonic waves reflected from surfaces can be made to interfere with itself thereby creating a standing wave thereby creating a well defined ultrasonic field at the same time avoiding creation of drifting/shifting fields of uncertain spatial and power distributions. In proposed arrangement an array of ultrasonic transducers are placed on inside of walls of the reactor and are reflected from a centrally placed reflector at center in place of commonly used stirrer of the circular reactor similar to a schematic shown below.



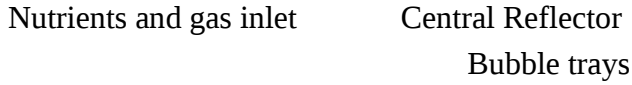


Figure 1
Schematic of an unstirred reactor using ultrasonic waves

Background of Formation of Standing Waves

Harmonic waves travelling in opposite directions can be represented by the equations below:

$$y_1 = y_0 \sin(kx - \omega t)$$

and

$$y_2 = y_0 \sin(kx + \omega t)$$

where:

- y_0 is the amplitude of the wave,
- ω (called angular frequency, measured in *radians per second*) is 2π times the frequency (in *hertz*),
- k (called the wave number and measured in *radians per meters*) is 2π divided by the wavelength λ (in *meters*), and
- x and t are variables for longitudinal position and time, respectively.

So the resultant wave y equation will be the sum of y_1 and y_2:

$$y = y_0 \sin(kx - \omega t) + y_0 \sin(kx + \omega t).$$

Using the trigonometric sum-to-product identity for 'sin(u) + sin(v)' to simplify:

$$y = 2\, y_0 \cos(\omega t)\, \sin(kx).$$

This describes a wave that oscillates in time, but has a spatial dependence that is stationary: sin(kx). At locations x = 0, λ/2, λ, 3λ/2, ... called the nodes the amplitude is always zero, whereas at locations x = λ/4, 3λ/4, 5λ/4, ... called the anti-nodes, the amplitude is maximum. The distance between two conjugative nodes or anti-nodes is λ/2.

Standing waves can also occur in two- or three-dimensional resonators. With standing waves on two-dimensional membranes such as drumheads, illustrated in the animations above, the nodes become nodal lines, lines on the surface at which there is no movement, that separate regions vibrating with opposite phase. These nodal line patterns are called Chladni figures. In three-dimensional resonators, such as musical instrument sound boxes and microwave cavity resonators, there are nodal surfaces.

Bubble size, nature of Cell suspension & Gas-Liquid mass-transport

Ultrasonic waves of 20 KHz have velocity of 1484 m/s in water and wavelength of 7.42 cm. This creates standing waves that have pitch of 3.71 cm. At these distances one would find low sound pressure interspersed with high pressures also separated by 3.71 cm from each other while these are separated from each other by 1.85 cm, when reactor volume is irradiated with ultrasound by transducers placed on insides of the reactor it is nicely divided laterally consequently into areas of high pressure- low cell concentration and low pressure- high cell concentration in presence of

medium intensity ultrasonic waves. A strategically placed physical screen at exit of that has openings at regularly paced distance of 0.5 cm each other would be able to prevent cell washout as long as liquid linear velocities stay low and below a certain linear velocity- critical velocity. Gases and nutrients are introduced at bottom of the reactor and enter these standing wave undergo compression –expansion from liquid lean in microbial concentration to areas with high microbial population where it is converted it is converted into useful end products that diffuse back equally efficiently to paths with high pressure- low cell population due to high diffusion coefficients of gases.

Reactors can be made in such a way that during each individual pass of gases only small % conversion of the feed takes place during an individual pass. Exiting gases from the reactors are treated with a sorbent/scrubbers that remove carbon dioxide and un-reacted gases are recycled back to inlet in each breath during each inhalation to maintain simplicity of design.

Whereas the observed ultrasound effect on solubility is very low (below 12%), it has been proved that ultrasound greatly improves gas liquid mass transfer, especially at gas induction speed, this improvement being further boosted by pressure. In typical conditions of organic synthesis: 323 K, 1100 rpm, 10 bar pressure *ka* is multiplied by 11 (3) when ultrasound is added to low speed mechanical stirring/agitation.

The influence of sonication is much higher (about fivefold in same conditions) on gassing out kinetics than on gassing in, except at very low stirrer speed (below 500 rpm) and at low gas induction/introduction/ gas flow rates. Moreover gassing out with ultrasound does not need mechanical stirring to be efficient and the presence of gas induced bubbles does not influence desorption mass transfer at all. Sonication (62.6 W for 1 liter nominal reactor volume) is the fastest way to degas an oversaturated liquid, even if the required energy is 17.6% higher than under mechanical stirring at 2000 rpm (4.95 W), desorption is twice faster under sonication (62.6 W) than under mixing at 2000 rpm (4.95 W).

Finally the use of ultrasound in autoclave reactor for enhancing gas–liquid mass transfer is very efficient even in absence of gas induction (=without much agitation). Indeed the presence of bubbles induction is not necessary to see an impact of sonication on mass transfer, even more in their presence enhancement observed by ultrasound diminishes. Ultrasound is thus a good tool to enhance gas–liquid mass transfer even at high pressure and temperature and even in absence of induced bubbles.

Ultrasonic waves are reflected from all discontinuities in phases and coupling of a wave of ultrasonic wave of wavelength λ to a particle of size α depends on matching of size of ultrasound wavelength and physical size of object power-transfer mismatch exists when dealing with these parameters of different orders, it being most efficient when these are comparable values. It is also affected by micro-structure of condensed phases. Many times inadvertently reflected radiation from different surfaces of the system creates standing/drifting fields of ultrasonic energy. Multiple reflections make prediction of accurate power levels of ultrasonic fields in a system difficult but these fields can be effectively controlled to spatially well defined areas and their levels spatially predicted if these beams are directed at each other and make to interfere with

itself creating a standing wave- a much preferable alternative due to certainties of distribution of the energy field. Formation of a standing wave also affects distribution of microbial cells. Cells migrate away from high energy field to low energy field. The migration and clumping and stability of the ensemble depend upon incident ultrasonic power and linear velocity of liquid flowing through the reactor. The ensemble of cells formed at low incident energy hold together till the linear velocity of liquid flowing through and between such ensembles exceeds a relatively low value that at higher incident power such ensembles hold out together till linear velocity of liquid exceeds a higher value. Actual value of linear velocities of liquid beyond which such self assembled cell formations have no stability are called critical velocities and depend upon cell type, temperature and viscosity of liquid. Use of this fact has been made to separate different cells by category (4).

Segregation of Microbial Mass Due to Ultrasound

One can visualize a reactor that has ultrasonic transducers installed on insides all along walls of the reactors parallel to the reactor axis in which ultrasonic reflectors fitted in place of a conventional stirrer that face each other directly and transducers operate in continuous mode. Gas and other nutrients are pumped in from reactor bottom with end products, liquid and gaseous flowing out from the reactor top with microbial mass withheld together due to its banding in areas of low ultrasonic energy due to presence of standing waves present and retained due to screen/s strategically placed towards section/reactor top that allow free flow of liquids but retain microbial mass. Such virtually formed cellular assemblies revert back to free flowing fluid once ultrasonic field is removed. Switching off/reduction of irradiation power for a certain liquid linear velocity facilitates removal/renewal of the cell mass/culture. Reactor consists of different zones of microbial cell distribution through which liquid containing nutrients and gas bubbles are pushed through liquid of low/no cell population in a reactor that has no conventional rotating stirrer. One necessary condition for the stability of such microbial cell ensemble is that linear velocity of liquid flowing through the reactor be lower than the characteristic critical velocity C_R. This arrangement achieves both purposes of virtual segregation of cellular mass and a factor of ten improvements in mass transport of gas/nutrients into/out of liquid in an unstirred reactor. Ingenious arrangement of ultrasonic arrays of transducers can be used for different arrangements of cellular masses or such arrays can be switched on/off in a time dependent manner so as to create effect of reactor stirrer rotation due to breaking/reformation of cellular masses during such time programmed switching.

Variation of Critical Flow rates with Cell Types (4)

Type of Cells	Energy density 1.6×10^{-5} J/s		Energy density of 2.5×10^{-5} J/s	
Yeast Cells	C_{RV}	C_{RL}	C_{RV}	C_{RL}
Wistar Rat Erythrocytes	0.04	0.034	0.7	0.0595
Guinea-pig erythrocytes	0.9	0.0765	1.4	0.119
	1.1	0.0935	1.7	0.145

C_{RV} is Critical Volume flow rate	C_{RL} is Critical linear velocity

Absorption of ultrasound energy depends upon matching of its wavelength with interacting objects, cellular objects do not absorb energy due to large mismatch between cells and ultrasound wavelength. This mismatch between ultrasonic wavelength and size of microbes and this is for a purpose. Ultrasonic waves are not meant to be exchanging energy with microbes as purpose is to improve mass transfer of gases in to the liquid that takes pace as a result of increase in diffusivities, so that both gassing-in and gassing-out is enhanced. Introduction of gases at the bottom of reactor creates bubbles and size of such bubble should preferably have a diameter similar to wavelength of the wave- about 7 cm. This also has upsetting microbial cell formations due to movement of bubbles that break and reform again after passage of bubble and exchange of gases further improving mass-transfer.

Kinetics of Interaction of Gas Bubbles with Cell Suspension in presence of Ultrasonic waves- Reversible Cell Cavitation

Application of ultrasound transiently permeabilizes cell membranes and offers a nonchemical, nonviral, and noninvasive method for cellular drug delivery (5). Although the ability of ultrasound to increase trans-membrane transport has been well demonstrated, a systematic dependence of transport on ultrasound parameters is not known. This study examined cell viability and cellular uptake of calcein using 3T3 mouse cell suspension as a model system. Cells were exposed to varying acoustic energy doses at four different frequencies in the low frequency regime (20–100 kHz). At all frequencies, cell viability decreased with increasing acoustic energy dose, while the fraction of cells exhibiting uptake of calcein showed a maximum at an intermediate energy dose. Acoustic spectra under various ultrasound conditions were also collected and assessed for the magnitude of broadband noise and subharmonic peaks. While the cell viability and transport data did not show any correlation with subharmonic (f/2) emission, they correlated with the broadband noise, suggesting a dominant contribution of transient cavitation. A theoretical model was developed to relate reversible and irreversible membrane permeabilization to the number of transient cavitation events. The model showed that nearly every stage of transient cavitation, including bubble expansion, collapse, and subsequent shock waves may contribute to membrane permeabilization. For each mechanism, the volume around the bubble within which bubbles induce reversible and irreversible membrane permeabilization was determined. Predictions of the model are consistent with experimental data.

Ultrasonic Irradiation and Cell Viability

Cell viability V_M and fraction of cells undergoing reversible permeabilization T_M can be shown to be related as follows; M being total number of transient cavitations

$T_M = V_M - e^{-\mu M}$

And

$M_{Max} = \ln(\lambda/\mu)/(\lambda-\mu)$

‘ $\lambda = 4/3\pi (r_1^3-R_b^3)(1/\eta)$ and $\mu= 4/3\pi (r_2^3-R_b^3)(1/\eta)$

‘ η is liquid volume

For reactors of very large volumes and operated at low gas induction rates with microbial cultures it is safe to make following assumptions

‘ $r_1 << R_b$; $r_2 > R_b$

Where r_1 is radius of microbial cell, R_b is bubble radius and r_2 is radius of volume not affected by cavitatation.

‘ $\lambda/\mu = [4/3\pi (r_1^3-R_b^3)(1/\eta)]/ [4/3\pi (r_2^3-R_b^3)(1/\eta)]$

$= -R_b^3/(r_2^3- R_b^3)$

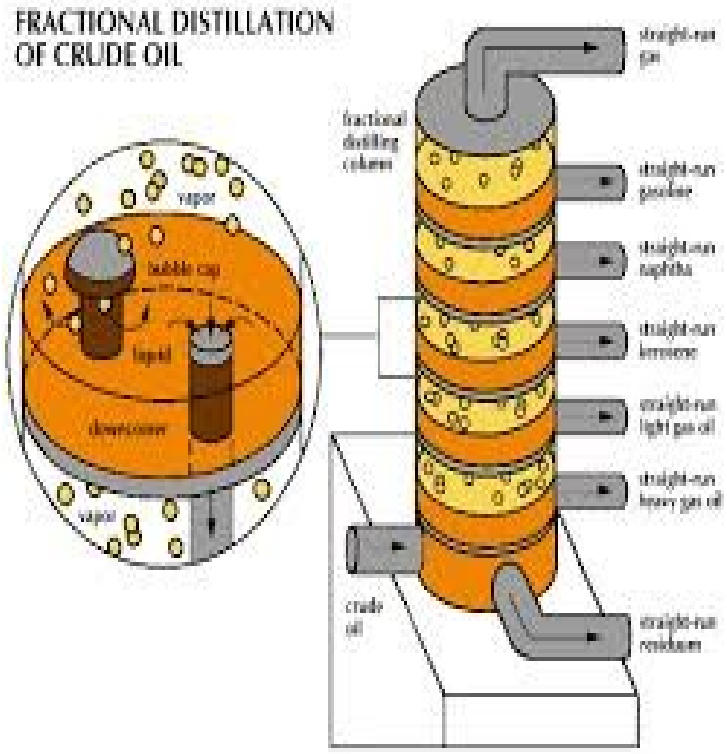
Under these conditions unless $R_b > r_2$, value of M is indeterminate. This reduces liquid that can be charged to reactor to less than 50 % of reactor volume at operating pressure. In other words volume occupied by bubbles at any time must be more than 50 % of reactor volume.

A reactor of nominal volume of 100 parts should hold liquid that is not more than 30 % of its capacity with 40 % being occupied by gas bubbles. Only in such cases reversible cavitation can take place due to ultrasonic waves. Such reactors are quite common and are known as bubble reactors commonly used in hydrogenation, alkylation and phosgenation. One pre-condition for benefiting from reversible cavitation is that volume of bubble is greater that volume of liquid hold up of the reactor. This fits well with our scheme of things but with one caveat that the gases exiting reactor be recycled after removal of end product like Carbon dioxide with an alkali scrubber. This also points to presence of large excess of Methane always present in the reactor. Such reactors have been modeed by K.Shimizu et al. (6)

Column Design Schematics

shown is one section of bubble reactor , multiple such sections are stacked together

Balanced flow fluidized liquid bubble reactor



Individual Bubble Tray Bubble Tray Stack

Bubble formers

Gas Flow Direction

Alternate structure of Bubble Tray

Gas pressure and flow is so adjusted that weight of liquid hold-up of the reactor is balanced by gas pressure in opposite direction. Reaction products are continuously removed from reactor side arm so that total liquid hold up of the reactor remains constant despite net production of liquid volumes from gaseous stream. Such volumes are subjected to refining to remove relatively volatile end products from aqueous stream also containing microbial cell culture.

Solubility of methane in water at atmospheric pressure is about 30 mg/L, for achieving desired mass transfer rate of 27 g/L/Hr under atmospheric conditions would need a volume of nearly 1000 L. Solubility of oxygen is 7.6 mg/L in water for Oxygen at 20^0 C at atmospheric pressure. It is about 28 mg/L at 4 Kg/cm2. At 10 Kg/cm2 pressure Methane solubility is expected to be 300 mg/L and Oxygen solubility of about 76 mg/L at 10 Kg/cm2.

Coming by to specific reaction mentioned in the challenge statement

$$5\ CH_{4(g)} + 4\ O_{2(g)} \rightarrow C_4H_{10}O_{(l)} + 5\ H_2O_{(l)} + CO_{2(g)}$$

There is large net conversion of gaseous volume to liquid product and due to this state of agitation would vary depending upon distance travelled by gaseous input in length of the bubble reactor. But as mentioned earlier during each of the conversions only a small % of input gases are converted during each single passage and this also ensures that activity coefficients of input gases remain unchanged over entire length of the reactor and state of agitation and level of mass transport remains roughly similar. It is a trick used by biological systems that nature has evolved during evolution. Carbon Dioxide being scrubbed from gases exiting the reactor and remaining gaseous stream recycled to inlet. Large quantities of gases exiting reactor also remove heat and does not require separate cooling jacket due to this. During passage of gases microbial culture undergoes repeated clustering due to presence of standing waves that are broken repeatedly by

passing gas bubbles that towards reactor exit forms stable clusters due to reduction in state of agitation as incoming gases are converted to liquid product. Reaction products are partially water miscible and of lower density that tend to accumulate at top of the reactor and can be gainfully removed as a reactor overflow that is rich in end product. Maintaining sufficiently low liquid linear velocities also retains bulk of microbial culture in the reactor due to screen placed at the top of the reactor to withhold cluster of microbial culture and break bubbles, multiple such screens can be placed in entire length of the reactor that segregates microbial culture into different sections that can be removed from such sections if such arrangements are in place.
As per S.S.Alves et al. (7) mass transfer coefficients in a mobile bubble reactors described above can be written as

‘ $k_L = 1.13\ (\alpha/d)^{1/2}\ D^{1/2}$

‘ α being bubble-liquid relative velocity (slip velocity), *d* being bubble diameter and D being gas diffusivity

Major improvements in mass-transfer are achieved due to improvements in gas diffusivity. Cell viability decreases due to cavitaion which in turn depends upon ambient pressure in reactor for ultrasound irradiation of given power. Higher pressures reduce intensity of cavitation and thus increase cell viability. Small bubble size give greater mass transfer coefficients, when large bubble enter high intensity ultrasonic field present in standing wave undergo compression and reduction in size and then break into large number of smaller bubbles as compressed bubble enters low pressure areas of standing wave also containing larger microbial cell population delivering reactants to cells and also removing Carbon Dioxide by out-gassing action of ultrasound.

The cavitation effects in ambient liquids are well-known and their application to conventional solvent extraction is well-established. However, when a liquid is pressurized, the acoustic intensity required to produce cavitation also increases and this generally places a natural limitation on application of ultrasonics to high-pressure processes. In ordinary solvents, cavitation does not occur at elevated pressures. To initiate the growth of a cavitation bubble, an acoustic pressure above the so-called Blake threshold pressure has to be applied.

During pressurization of a liquid, the Blake threshold pressure increases, which imply that higher acoustic pressures are needed to produce cavitation. Obviously, no cavitation occurs when the Blake threshold pressure exceeds the maximum acoustic pressure. These authors argue that the high vapor pressure and low surface tension of the fluid counteracts the external pressure applied. They demonstrated that the threshold pressure of liquid CO_2 at 5.82 MPa is equal of the threshold pressure of water at 0.1 MPa and 20°C. It is observed that the cavitation collapse of a bubble was not strong enough to create hot-spots for monomolecular conversion in bulk free-radical polymerization of methyl methacrylate using CO_2.

Although cavitation has thus been established in near-critical carbon dioxide, the absence of phase boundaries would appear to prohibit bubble formation above the critical point. This would imply that rate enhancement of supercritical fluid extraction (SFE) process can occur only through the turbulence associated with acoustic streaming or through simple mechanical vibration.

Variation in Mass-Transport rates with Nature of Bubbles in Stream

As per experimental data presented in ref (7) on the average mass transfer liquid film coefficient, k_L, in an aerated stirred tank range from those expected for bubbles with a mobile surface, $k_{mobileL}$, to those expected for rigid bubbles, k_{RigidL} which are much lower. Bubbles in Poly Ethylene Glycol solution behave as rigid bubbles, while bubbles in tap water behave closer to having a mobile interface.

Bubbles in salt solution have intermediate values of k_L. For the same liquid medium (salt solution) smaller bubbles result in lower values of k_L, closer to k_{RigidL}.

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Gas-Liquid Mass-Transfer Data for stirred Bubble Reactors without application of Ultrasound

Data From Ref (7)

Conditions	Location	ε	$d32$ (m)	a (m−1)	x	KL (ms−1)	kLa (s−1)
S-N2-Q1	Top	0.031	0.00167	110 0	0	0.000078	0.0085
	Bottom	0.013	0.00164	46	0.62	0.000401	0.0184
S-N4-Q1	Top	0.053	0.00122	269	0	0.000085	0.0229
	Bottom	0.033	0.00128	157	0.73	0.000198	0.0310
S-N4-Q2	Top	0.069	0.00144	285	0	0.00082	0.0233
	Bottom	0.035	0.00120	175	0.67	0.000291	0.0509
PEG-N4-Q1	Top	0.060	0.00125	307	0	0.000084	0.0259
	Bottom	0.039	0.00116	198	0	0.000086	0.0170

‘Condition’ – Refers to a type of Liquids present in reactor volume differing mainly in ionic strength or viscosity in a similarly dimensioned reactor volumes

Terminology used as per (7) or as below

a specific interfacial area based on the liquid volume (m−1)

c constant

C concentration (mol m−3)

d, *d*32 bubble diameter, Sauter mean diameter (m)

D gas diffusivity in the liquid (m2 s−1)
ε is the overall gas holdup
*h*trans height of the clean segment at the bubble front (m)
k constant (mole m/L/ s)
*k*L liquid-side mass transfer coefficient (m s−1)
*k*L*a* volumetric mass transfer coefficient referred
to the liquid volume (s−1)
n number of bubbles
N agitation rate (s−1)
Q gassing rate (m3 s−1)
Q peroxide peroxide solution addition flow rate (mol s−1)
t time (s)
*t*R residence time (s)
V volume (m3)
‘ *x* – fraction of bubbles that are mobile (= t_{mobile}/t_R)

Measured value of k_L in Stirred Bubble reactors without use of Ultrasound

It is clear from the data that mass-transfer coefficients vary depending upon distance of bubbles from the reactor walls, type of liquid and operating conditions. High values as much as 0.0509/s can be achieved for Nitrogen gas that has similar solubility as methane and oxygen in water, converted into /Hr we get value of 183.24 at high end and 30.6 at lower end. This is entirely in range specified in challenge requirements.

Efficiencies in Unstirred Bubble reactors with use of ultrasound

Bubble reactors when used with ultrasound increase these by a factor of ten higher than the data presented in the table. This allows very efficient gas-liquid mass-transport as desired. It also allows for reduction in reactor sizes or for achieving higher throughput in existing reactor systems.

Intensity of Power Consumption

Work done by authors (8) with miniature (2 mL) and laboratory-scale (100 mL) bubble column bioreactors useful for the cultivation of microbial cells provide useful data on power consumption. These bioreactors were constructed of glass and used a range of sintered glass gas diffusers with differently sized pores to disperse humidified air within the liquid bio-medium. The effect of the pressure of this supplied air on the breakthrough point for gas diffusers with different pore sizes was examined and could be predicted using the Laplace-Young equation. The influence of the superficial gas velocity (*u*g) on the volumetric mass transfer coefficient (*k*L*a*)

was determined, and values up to 0.09/ s were observed in this work. Two modeling approaches were considered in order to predict and provide comparison criteria. The first related the volumetric power consumption (*P*/*V*) to the *k*L*a* and a good correlation was obtained for differently sized reactors with a given pore size, but this correlation was not satisfactory for bubble columns with different gas diffusers. Values for *P*/*V* ranged from about 10 to400 W,m-3. Second, a model was developed predicting bubble size (*d*b), bubble rising velocity (*u*b), gas hold-up (_), liquid side mass transfer coefficient (*k*L), and thus the *k*L*a* using established theory and empirical correlations. Good agreement was found with our experimental data at different scales and pore sizes. Values for *d*b varied from 0.1 to 0.6 mm, and *k*L values between 1.7 and 9.8 × 10-4 m.s-1 were determined. Several *E. coli* cultivations were performed in the miniature bubble column at low and high *k*L*a* values, and the results were compared to those from a conventional stirred tank operated under identical *k*L*a* values. Results from the two systems were similar in terms of biomass growth rate and carbon source utilization. Add to this power 500 W/m3 consumption due to ultrasonic transducers thus adds up to **1 KW/m3**. This is a factor of ten lower than the challenge requirements. Since microbial culture is confined to a certain area and not dispersed throughout reactor volume, flow of gas through areas lean in culture is expected to experience lower resistance and thus result in reduced power consumption. The power consumption figures are based on gas introduction through sintered frit. It is envisaged that gas introduction be done with use arrangement similar to distillation columns with bubble trays. It is expected that this arrangement is not as efficient but satisfies major requirements of the application.

References

(1)Sinisterra JV Ultrasonics. 1992;30(3):180-5.
(2)Yusuf Chisti Trends in Biotechnology Volume 21, Issue 2, February 2003, Pages 89–93

*(3)Laugier F. et al. **Ultrason Sonochem.** 2008 Sep;15(6):965-72. doi: 10.1016/j.ultsonch.2008.03.003. Epub 2008 Mar 17.*

(4) Diana Sadikova et al. ***Open Journal of Biophysics*, 2013, 3, 70-75** http://dx.doi.org/10.4236/ojbiphy.2013.31A009 Published Online February 2013 (http://www.scirp.org/journal/ojbiphy)

(5) Jagannathan Sheshadri et al. Biophysical Journal Volume 84 May 2003 3087–3101

(6) Shimizu, K.; Takada, S.; Minekawa, K.; Kawase, Y., Phenomenological model for bubble column reactors: prediction of gas hold-ups and volumetric mass transfer coefficients. Chem. Eng. J. 2000, 78, (1), 21-28

(7) S.S.Alves et al. Chemical Engineering and Processing 43 (2004) 823–830

(8) Steven D. Doig et al. Biotechnol. Prog. **2005,** 21, 1175−1182